

Topic 18: Organic Chemistry – Arenes

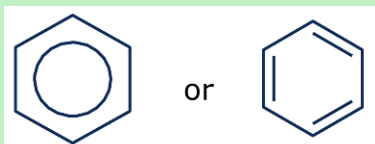
Knowledge of the common uses of organic compounds mentioned in this topic is expected.

Students will be assessed on their ability to:

18.1

be able to use thermochemical, X-ray diffraction and infrared data as evidence for the structure and stability of the benzene ring

Students may represent the structure of benzene as



as appropriate in equations and mechanisms.

Organic Compounds

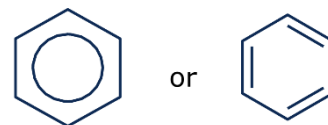
Aliphatic (Non-cyclic/ Open chain)
straight or branched chain hydrocarbons

Aromatic (Arene/ Closed Chain)
hydrocarbon ring with delocalized
electrons forming pi bonds in the ring

!Benzene belongs in the aromatic class

Benzene's Structure

- Simplest arene is benzene (molecular formula C_6H_6)
- Basic structure is six C atoms in a hexagonal ring, with one H atom bonded to each C atom



A little backstory on how we arrived at this new model of structure and stability of the benzene ring

Problem 1: Shouldn't benzene decolourise bromine water in an addition reaction if it has $C=C$ double bonds?

Ans: There are no individual $C=C$ bonds, so no reaction with bromine

Problem 2: Shouldn't there be 4 isomers of $C_6H_4Br_2$ according to Kekule structure?

Ans: There are only three because when the Br atoms are on adjacent atoms, there is no difference in the arrangement of electrons between these atoms

Problem 3: Evidence from X-ray diffraction about the lengths of covalent bonds in molecules suggests that the carbon-carbon bonds in benzene are all the same, why?

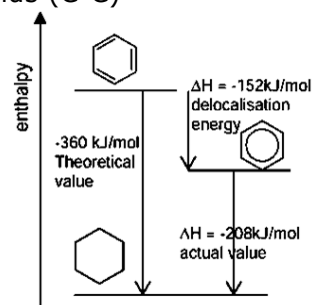
Ans:

BOND	BOND LENGTH/pm
C–C in cyclohexene	154
C=C in cyclohexene	134
C–C in benzene	139

The bonds are the same length as they are identical
Electrons are evenly distributed throughout the ring
Kekule structure would have shorter double bonds ($C=C$) and longer single bonds ($C-C$)

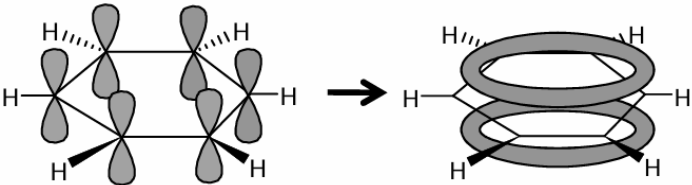
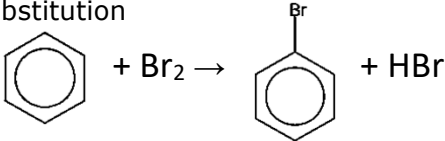
Problem 4: Evidence from thermochemical data about enthalpy changes of hydrogenation suggests this diagram, why?

Ans: When charge is spread across in a species, there is increased stability, which explains the 152kJ/mol greater stability of benzene compared with cyclohexa-1,3,4-triene

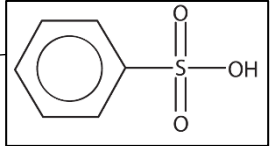


Problem 5: Evidence from infrared spectra of cyclohexene and benzene

Ans: IR spectrum of benzene has a very strong absorption at 1500 cm^{-1} which is typical of $C=C$ in an aromatic compound (Absorptions for $C=C$ in non-aromatic compounds are between 1680 and 1645 cm^{-1})

	Arenes have high melting points due to the high stability of the delocalised benzene ring, but low boiling points as they are non-polar molecules and generally cannot be dissolved in water
18.2	understand that the delocalised model for the structure of benzene involves overlap of <i>p</i> -orbitals to form π -bonds
	<p>Delocalized Model for Structure of Benzene</p> <ul style="list-style-type: none"> - Each C atom is bonded to two other C atoms and one H atom by single covalent sigma-bonds which leaves one delocalised electron on each C atom in a <i>p</i>-orbital, perpendicular to the plane of the ring - The six delocalized electrons in <i>p</i>-orbitals overlap in a ring structure above and below the plane of carbon atoms to form pi-bonds - Benzene is a <i>planar molecule</i> (The evidence suggests all the C-C bonds are the same and have a length and bond energy between a C-C single and C=C double bond) 
18.3	understand why benzene is resistant to bromination, compared to alkenes, in terms of delocalisation of π -bonds in benzene compared to the localised electron density of the π -bond in alkenes
	<p>Benzene <i>does not generally undergo addition reactions</i> (bromination addition)</p> <ul style="list-style-type: none"> - This is because these would involve breaking up the delocalised system (the delocalization of pi-bonds) unlike in alkenes where the electron density of the pi-bonds is localized - Hence, most of benzene's reactions are substitutions of one H for another atom or group of atoms - And since benzene has a high electron density and so attracts electrophiles, it mostly undergoes electrophilic substitutions
18.4	<p>know the following reactions of benzene, limited to:</p> <ol style="list-style-type: none"> oxygen in air (combustion to form a smoky flame) bromine, in the presence of a catalyst a mixture of concentrated nitric and sulfuric acids fuming sulfuric acid halogenoalkanes and acyl chlorides with aluminium chloride as catalyst (Friedel Crafts reaction)
i	<p>Reactions with oxygen (Combustion)</p> <p>Benzene + Oxygen → Carbon Dioxide + Water</p> $\text{C}_6\text{H}_6(\text{l}) + 7.5\text{O}_2 \rightarrow 6\text{CO}_2 + 3\text{H}_2\text{O}$ <p>Benzene will burn in a smoky/ sooty flame</p> <p>The lower the carbon to hydrogen ratio, the sootier the flame</p> <div style="border: 1px solid black; padding: 5px; width: fit-content; margin-left: auto;"> <p>Test for aromatic compounds</p> <p><i>smoky flames</i> indicate a positive test</p> </div>
ii	<p>Halogenation of Benzene</p> <p>Mechanism: Electrophilic substitution</p> <div style="text-align: center;">  </div> <p>Change in functional gp. Benzene Bromobenzene</p> <p>Reagents: FeBr₃ catalyst (or AlBr₃)</p> <p>Conditions: Heat under reflux with halogen carrier (catalyst)</p> <div style="border: 1px solid black; padding: 5px; width: fit-content; margin-left: auto;"> <p>Same for reaction with chlorine (catalyst can be AlCl₃ or FeCl₃)</p> </div>

FeBr₃ can be made by reacting Fe with Br₂

iii	<p>Nitration</p> <p>Mechanism: Electrophilic substitution</p> $\text{C}_6\text{H}_6 + \text{HNO}_3 \rightarrow \text{C}_6\text{H}_5\text{NO}_2 + \text{H}_2\text{O}$ <p>Change in functional gp. Benzene Nitrobenzene</p> <p>Reagents: Conc. HNO_3 in presence of conc. H_2SO_4 (Catalyst)</p> <p>Conditions: Warm with reagents and catalyst at $50\text{--}60^\circ\text{C}$</p>
iv	<p>Sulfonation</p> <p>Electrophile: SO_3 (fuming H_2SO_4 is SO_3 dissolved in conc. H_2SO_4)</p> <p>Mechanism: Electrophilic substitution</p> $\text{C}_6\text{H}_6 + \text{H}_2\text{SO}_4 \rightarrow \text{C}_6\text{H}_5\text{SO}_3\text{H} + \text{H}_2\text{O}$  <p>Change in functional gp. Benzene Sulfonated benzene</p> <p>Reagents: Fuming concentrated H_2SO_4</p> <p>Conditions: Heat under reflux at 40°C for at least 30 minutes (several hours)</p>
v	<p>Friedel-Crafts Reactions</p> <p>Type: Alkylation</p> <p>Mechanism: Electrophilic substitution</p> $\text{C}_6\text{H}_6 + \text{CH}_3\text{CH}_2\text{Cl} \rightarrow \text{C}_6\text{H}_5\text{CH}_2\text{CH}_3 + \text{HCl}$ <p>Change in functional gp. Benzene Alkylbenzene</p> <p>Reagents: RCl (chloroalkane) in presence of anhydrous AlCl_3 catalyst</p> <p>Conditions: Heat under reflux</p> <hr/> <p>Type: Acylation</p> <p>Mechanism: Electrophilic substitution</p> $\text{C}_6\text{H}_6 + \text{CH}_3\text{COCl} \rightarrow \text{C}_6\text{H}_5\text{COCH}_3 + \text{HCl}$ <p style="text-align: center;">phenylethanone Phenyl Ketone</p> <p>Change in functional gp. Benzene</p> <p>Reagents: Acyl chloride in presence of anhydrous AlCl_3 catalyst</p> <p>Conditions: Heat under reflux (50°C)</p>

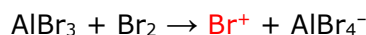
18.5

understand the mechanism of the electrophilic substitution reactions of benzene in halogenation, nitration and Friedel-Crafts reactions, including the generation of the electrophile

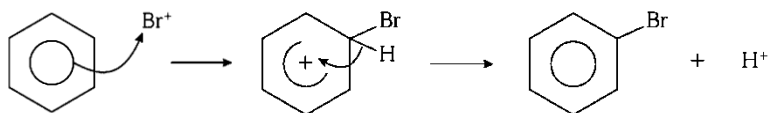
Electrophilic Substitution Mechanism

Halogenation

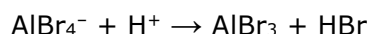
Step 1: Formation of the electrophile



Step 2+3: Electrophilic attack + Formation of the aromatic product



Step 4: Regeneration of the catalyst

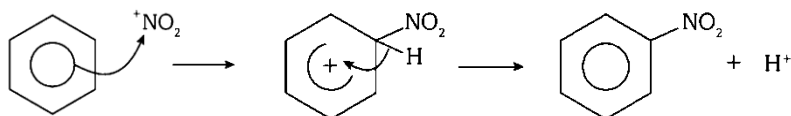


Nitration

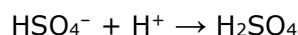
Step 1: Formation of the electrophile



Step 2+3: Electrophilic attack + Formation of the aromatic product

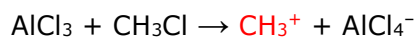


Step 4: Regeneration of the catalyst

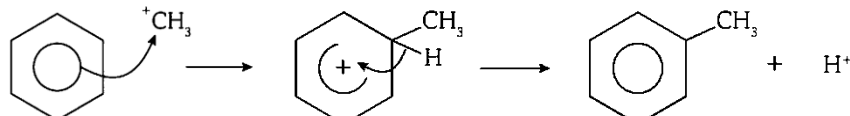


Alkylation

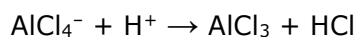
Step 1: Formation of the electrophile



Step 2+3: Electrophilic attack + Formation of the aromatic product

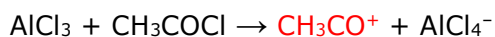


Step 4: Regeneration of the catalyst

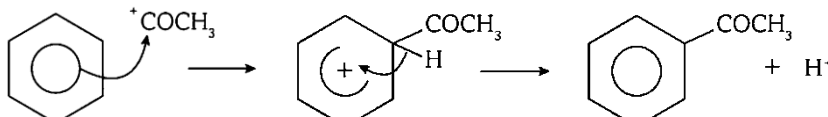


Acylation

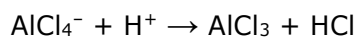
Step 1: Formation of the electrophile



Step 2+3: Electrophilic attack + Formation of the aromatic product



Step 4: Regeneration of the catalyst



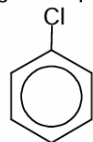
Effect of side groups on benzene ring

- Electron releasing side groups such as alkyl groups, phenols and amines releases electrons into the delocalised system and so increasing the electron density in the ring and making it more attractive to electrophiles
- Hence, their substitution reactions occur more readily with milder conditions

This reaction is done at 60°C. On using higher temperatures a second nitro group can be substituted onto different positions on the ring

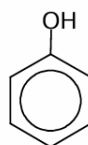
Effect of delocalisation on side groups with lone pairs

If a -OH group, a Cl atom or an NH₂ group is directly attached to a benzene ring the delocalisation in the benzene ring will extend to include the lone pairs on the N, O and Cl. This changes the properties and reactions of the side group



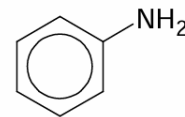
chlorobenzene

The C-Cl bond is made stronger. Typical halogenoalkane substitution and elimination reactions do not occur. Also the electron rich benzene ring will repel nucleophiles



phenol

Delocalisation makes the C-O bond stronger and the O-H bond weaker. Phenol does not act like an alcohol- it is more acidic and does not oxidise



phenylamine

Less basic than aliphatic amines as lone pair is delocalised and less available for accepting a proton

18.6

understand the reaction of phenol with bromine water and the reasons for the relative ease of this reaction compared to benzene

Phenols

- A phenol consists of a hydroxy (-OH) group directly attached to a benzene ring (Note that the -OH group should be attached to the benzene ring and not an alkyl group, to be considered as a phenol)
- Phenols are very weakly acidic (They are weaker acids than carboxylic acid)
- Both phenols and carboxylic acids will react with Na metal and NaOH
- Only carboxylic acids will react with Na₂CO₃ as a phenol is not strong enough an acid to react

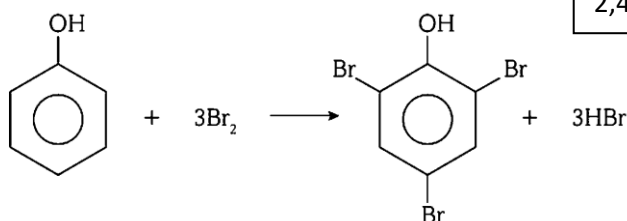
Bromination of Phenol (Test for phenol)

Reagents: Bromine water

Type: Electrophilic substitution

Conditions: Room temperature

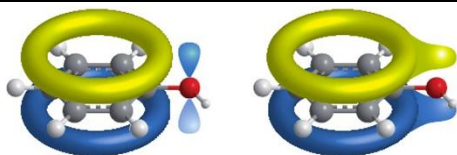
Phenol **decolourises** the **orange** bromine solution to form a **white precipitate** of 2,4,6-tribromophenol



2,4,6-tribromophenol (white solid)

Compared to bromination of benzene,

- Phenol does not need a catalyst, occurs at room temp. (no need to be heated under reflux) and undergoes multiple substitution (3 substitutions)
- The lone pair of electrons on the oxygen in phenol overlaps with the delocalised pi electron system of the benzene ring, increasing its electron density and making it more susceptible to electrophilic attack

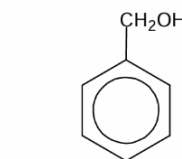


▲ **fig A** The electrons in the p_z-orbital of the oxygen atom become part of the delocalised electron system. This increases the electron density above and below the ring and makes the molecule more attractive to electrophiles such as Br⁺.

Phenols are used in the production of plastics, polymers, antiseptics, disinfectants and resins for paints

Further suggested practical:

Carry out the reactions in 18.4, and 18.6 where appropriate (using methylbenzene or methoxybenzene)



This is not a phenol, but is an alcohol because the OH group is attached to an alkyl group rather than the benzene ring.